in the calculation. However, the variations in σ and π bonding within a given molecule would not be expected to be nearly as sensitive to parameterization. A separate calculation was done adjusting the equatorial lengths to 1.900 Å for Cr–C and 1.13 Å for C–O to match the axial distances with the expectation that the only significant effect would be in the equatorial Cr–C π bonding. This was confirmed; the Cr–C σ contributions were again nearly equal (0.326 equatorial and 0.321 axial) but the equatorial π contribution was reduced to 0.327, still slightly greater than the axial π contribution of 0.304. Thus, the only significant difference on forcing equivalent equatorial and axial bond lengths was a decrease in the equatorial Cr–C π bonding. The implication is that in $(CO)_4CrB_3H_8^-$ the 0.08-Å difference between axial and equatorial Cr–C distances results from increased π bonding in the equatorial Cr–C bonds. As the Cr–C overlap increases, the C–O overlap decreases; this, too, is reflected in the observed carbonyl C–O distances.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA 32306

Metal Carbonyl–Trifluorophosphine Systems. VIII. Spectral Studies and the Fluxional Nature of Butadienetricarbonyliron(0)

BY J. D. WARREN AND RONALD J. CLARK

Received August 18, 1969

Butadienetricarbonyliron(0) undergoes photochemical or thermal exchange with ^{13}CO and substitution with PF_3. Very little butadiene replacement occurs. Cotton–Kraihanzel type force constant calculations have been made on the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species. The carbonyl force constants for the tricarbonyl have been determined and these constants can be used to calculate all ^{13}CO frequencies. Those up through dicarbonyl-^{13}C have been verified by isotopic enrichment. The tricarbonyl moiety has one unique carbonyl position which is occupied by PF_3 on substitution. Low-temperature fluorine nmr confirms the nonequivalence of the three positions in $C_4H_6Fe(CO)(PF_3)_2$. At room temperature, the nmr spectra of $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ show a time-averaged equivalence indicating some form of fluxional nature in the structure. It is suggested that this is a rotational motion comparable to the Bailar twist.

Introduction

Butadienetricarbonyliron(0), $C_4H_6Fe(CO)_3$, is one of the earlier known organometallic compounds,[1,2] yet its spectral properties and substitution reactions have received only limited attention.

The tricarbonyl was reported by Pauson[2] to have two stretching vibrations in the carbonyl region. This can lead to the assumption that the tricarbonyl portion possesses C_{3v} symmetry. This symmetry does not agree with the X-ray structure, however.[3] More recently, higher resolution infrared spectrometers have shown the presence of three carbonyl vibrations rather than two[4] indicating that the symmetry is indeed lower than C_{3v}.

Only limited studies have been made concerning the reactions of $C_4H_6Fe(CO)_3$ with neutral ligands. In these reactions, either the diene or the carbonyl groups can be replaced. Both reactions have been observed. For instance, it has been reported that triphenylphosphine reacts thermally with $C_4H_6Fe(CO)_3$ to yield $Fe(CO)_2[P(C_6H_5)_3]_3$[5] whereas photochemically these compounds react to yield $C_4H_6Fe(CO)_2P(C_6H_5)_3$, $C_4H_6Fe(CO)[P(C_6H_5)_3]_2$, $Fe(CO)_3[P(C_6H_5)_3]_2$, and an unidentified red product.[6]

To further the understanding of $C_4H_6Fe(CO)_3$, additional studies have been undertaken. These studies include detailed force constant calculations on the tricarbonyl utilizing its ^{13}CO-enriched analogs. They also include a study of the reaction products of $C_4H_6Fe(CO)_3$ with PF_3 and a subsequent proton and fluorine nmr investigation of the resulting $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ products.

The use of phosphorus trifluoride as a ligand was particularly revealing. Past studies[7] have shown that PF_3 and CO are so similar as ligands that they substitute quite freely for one another with very little change in either the physical properties or the bonding. However, PF_3 is quite amenable to nmr study whereas carbonyl groups are not.

From these studies have come an unexpected example of a fluxional compound.

Experimental Section

Butadieneiron tricarbonyl was obtained from Alfa Inorganics. It was sufficiently pure to be used as received or as it was after simple vacuum distillation. Its properties were unchanged upon gas–liquid partition chromatographic purification.

---

[1] H. Reihlen, A. Grahl, G. v. Hessling, and O. Pfrengle, *Ann.*, **482**, 161 (1930).

[2] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

[3] O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 241 (1960); O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963).

[4] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

[5] T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

[6] F. M. Chaudhari and P. L. Pauson, *J. Organometal. Chem.* (Amsterdam), **5**, 73 (1966).

[7] C. A. Udovich and R. J. Clark, *Inorg. Chem.*, **8**, 938 (1969), and earlier papers in the series; Th. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967).

Enrichment with ^{13}CO was performed by irradiating 0.1 ml of $C_4H_6Fe(CO)_3$ in 0.5 ml of heptane under an environment of 55 mole % ^{13}CO (Merck Sharp and Dohme of Canada, Ltd.) A Pyrex vessel of 6-ml capacity was used for the irradiation. It was equipped with a silicone rubber septum so that samples could be removed periodically for infrared examination. The vessel was irradiated by an AH-6 1000-W General Electric uv lamp. The ^{13}CO atmosphere was replaced once during the course of 60 hr of irradiation.

Three basic techniques were used for the production of $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ mixtures. In the first technique, a thermal reaction was used in which 0.5 ml of $C_4H_6Fe(CO)_3$ was placed in a 150-ml pressure vessel and sufficient PF_3 was added to yield a pressure of 200 psi. This vessel was heated to 140° for 18 hr. In order to produce quantities of the more extensively substituted product, the vessel was cooled to $-196°$, the evolved CO was pumped off, and the vessel was reheated. This process was repeated up to five times. The amount of CO evolved dropped rapidly through the cycles.

The second technique was a photochemical reaction. About 0.5 ml of $C_4H_6Fe(CO)_3$ in 5 ml hexane was placed into a 500-ml flask along with sufficient PF_3 to yield a pressure of about 600 Torr. The vessel was irradiated at room temperature by an AH-6 lamp for 5–18 hr with the evolved CO being removed periodically at $-196°$ by vacuum pumping.

In the final method, 3.0 ml of $Fe(PF_3)_x(CO)_{5-x}$[8] ($x = 3$–4) and 10 ml of liquid C_4H_6 were placed in a pressure vessel. The vessel was heated to 120° for 24–36 hr. The excess C_4H_6 and $Fe(PF_3)_x(CO)_{5-x}$ were removed by subjecting the product to a vacuum of about 0.1 Torr for a few minutes at room temperature. The main product was removed by either prolonged pumping at room temperature or by a solvent like hexane. This method has not been fully developed, but it shows promise of being the one capable of giving the greatest yield of higher substituted $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species. Higher temperatures (>150°) or prolonged heating yielded large quantities of a rubbery polymer from the butadiene.

These mixtures were separated on a Varian Aerograph A-700 preparative gas–liquid partition chromatograph. A 4 m × 0.25 in. 15% DC-702 silicone oil column on Chromosorb FB was used. The temperature was 80° and the helium flow was 50 cm^3/min. The compounds were trapped at either 0 or $-78°$.

Infrared spectra were run in hexane on a Perkin-Elmer 521. The spectrum of the hydrocarbon portion was determined in CCl_4. The spectrometer was calibrated in the carbonyl region with gaseous DCl[9] during runs recorded on an expanded wave number scale. The accuracy of the values for the carbonyl bands is felt to be ± 0.3 cm^{-1}.

The proton and fluorine nmr spectra were determined on a flux-stabilized HA-60 Varian spectrometer at 60 and 56.4 MHz, respectively. The compounds $CHCl_3$ and $CFCl_3$ were used for internal lock and as standards for the respective spectra. In addition to $CHCl_3$ and $CFCl_3$, CS_2 was added as solvent.

Results

Both ^{13}CO exchange and PF_3 substitution occur as closely related processes. These reactions are relatively slow. In the photochemical reaction, only carbonyl replacement has been detected, but in the thermal process, a few per cent of the $Fe(PF_3)_x(CO)_{5-x}$ species are found. These species are readily identified by comparing their infrared spectra and particularly their glpc patterns (on a 7-m column) with that of an authentic sample.[8] Obviously, x is always 2 or greater in the $Fe(PF_3)_x(CO)_{5-x}$ that is produced.

The butadieneiron–carbonyl–trifluorophosphine compounds $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ are identified by a variety of techniques.

(1) **Order of Formation.**—Since the mono-, di- and trisubstituted species would be expected to be formed sequentially, the species can be tentatively identified by a study of their order of formation. This is accomplished by examining the spectral properties as a function of time.

(2) **Order of Elution.**—The retention times of the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species increase as x increases. This is the order of elution found in almost all metal carbonyl–trifluorophosphine systems that have been studied to date.

(3) **Mass Spectroscopy.**—Parent ion molecular weights agree with the expected values. Also, the sequential loss of CO groups and PF_3 groups can be seen as expected.

(4) **Infrared Spectra.**—The infrared spectra of the C–H stretching and olefinic regions indicate that no significant change has occurred from the parent compound. In addition, P–F vibrations appear, and the carbonyl region changes in a manner predictable by group theory. The carbonyl spectra for the species are shown in Table I.

Table I

Observed Infrared Spectra of the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ Species in the Carbonyl Region (cm^{-1})

$C_4H_6Fe(CO)_3$	$C_4H_6Fe(CO)_2(PF_3)$
2055.7 s	2031.6 s
1989.8 s	1981.0 s
1979.9 s	2017.6 w
2045 sh, w	1950.1 w
1956.3 w	
1945.9 w	$C_4H_6Fe(CO)(PF_3)_2$
	2001.4 s
	1956.3 w

(5) **Proton Nmr.**—The proton nmr spectra of the species resemble that of the parent. The proton spectra of the parent as well as all of the substituents have absorptions in the $\delta = 0$, 2, and 6 regions relative to TMS. The main difference in the spectra of the phosphine species relative to the tricarbonyl is that the spectra are more complex and less well resolved due to phosphorus coupling.

(6) **Fluorine Nmr.**—All species show two regions of resonance separated by about 1300 Hz. This is what is expected of coordinated PF_3. The monophosphine is a simple doublet ($J_{PF} = 1300$ Hz) and the spectra of the diphosphine and triphosphine become more complex. These spectra will be discussed in greater detail later.

These compounds are stable yellow solids with low melting points. They transfer under high vacuum at room temperature and are fairly stable. There is very little tendency to disproportionate. They are stable in nonhydroxylic organic solvents such as hydrocarbons, benzene, and chloroform.

Force Constants.—The general structure[3] of $C_4H_6Fe(CO)_3$ is shown in Figure 1. This structure can be

---

[8] R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964); C. A. Udovich, R. J. Clark, and H. Haas, *ibid.*, **8**, 1066 (1969).

[9] IUPAC Commission on Molecular Structure and Spectroscopy, *Pure Appl. Chem.*, **1**, 582 (1961).

described as a square-pyramidal arrangement with the iron raised about 0.2 Å above the basal plane.

Force constants have been calculated by the basic Cotton–Kraihanzel technique.[10] The carbonyl groups have two stretching force constants K_1 and K_2 for carbonyls 1 and 2 or 2′, respectively, and two interaction force constants K_{12} and $K_{22'}$ correspondingly defined. Since there are only three ^{12}CO carbonyl bands, the calculation of these four constants requires either the assumption of some relationship between the various constants or the use of additional data. Both procedures have been used by various workers in other studies, but it is generally desirable to obtain more data *via* the natural and enriched ^{13}CO species.[11]

Since there will be several possible sets of assignments that yield real roots to the equations, it is desirable to attempt to predict in advance the relative magnitude of the stretching force constants and interaction constants in order to aid in the choice of the best set of assignments.

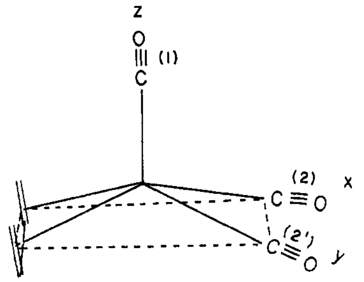
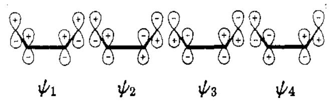


Figure 1.—Structure of $C_4H_6Fe(CO)_3$. The letters x, y, and z refer to the axes used in naming the orbitals.

In a tetragonal pyramid such as shown in Figure 1, metal orbitals which are appropriate for forming σ-hybrid orbitals are ns, np$_x$, np$_y$, $(n-1)$d$_{z^2}$, and $(n-1)$d$_{x^2-y^2}$. (The orbital p$_z$ is also of appropriate symmetry, but the envolvement of p$_z$ will surely be less than that of d$_{z^2}$.) The remaining orbitals d$_{xy}$, d$_{xz}$, d$_{yz}$, and also p$_z$ are of appropriate symmetry for π bonding.

The Hückel molecular orbitals for butadiene[12] are



The doubly occupied orbitals ψ_1 and ψ_2 are of appropriate symmetry for σ donation and ψ_3 and ψ_4 are appropriate for π acceptance from filled metal orbitals.

Table II

Carbonyl	π bonds with	With competition from
$(CO)_1$	d$_{xz}$	$(CO)_2$, ψ_3, ψ_4
	d$_{yz}$	$(CO)_{2'}$, ψ_3, ψ_4
$(CO)_2$	d$_{xz}$	$(CO)_1$, ψ_3, ψ_4
	d$_{xy}$	$(CO)_{2'}$
	p$_z$	$(CO)_{2'}$, ψ_3
$(CO)_{2'}$	d$_{yz}$	$(CO)_1$, ψ_3, ψ_4
	d$_{xy}$	$(CO)_2$
	p$_z$	$(CO)_2$, ψ_3

The orbitals of appropriate symmetry for π bonding with the various carbonyls and the groups that compete with the carbonyls for these orbitals are listed in Table II. Carbonyl 1 must compete with another carbonyl plus butadiene for the π-bonding electrons of both the d$_{xz}$ and the d$_{yz}$ orbitals. Likewise, carbonyl 2 must compete with carbonyl 1 and with butadiene for the π-bonding electrons of d$_{xz}$, but only with carbonyl 2′ for the π electrons of d$_{xy}$. A similar situation holds for carbonyl 2′. In addition, to whatever extent p$_z$ is involved in π bonding, it will bond with carbonyls 2 and 2′. The net effect will be greater π bonding of the metal with carbonyls 2 and 2′ than with carbonyl 1. This results in a lower C–O bond order for carbonyls 2 and 2′ than for carbonyl 1. Thus, on the basis of these arguments, one would expect $K_1 > K_2$.

By a related argument, one can make a prediction about the relative magnitudes of the interaction constants. When carbonyl 2 stretches, there is an increase of the electron density in the d$_{xz}$ and d$_{xy}$ orbitals. The d$_{xz}$ orbital is used in π bonding to carbonyl 1 and to butadiene, whereas d$_{xy}$ is used only in π bonding to carbonyl 2′. Hence, when carbonyl 2 stretches, it has a greater effect on carbonyl 2′ than on carbonyl 1, leading to a prediction of $K_{22'} > K_{12}$.

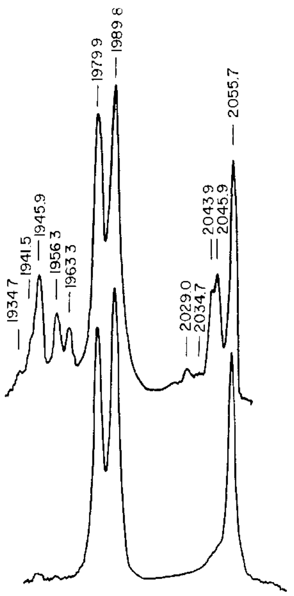


Figure 2.—Representative infrared spectra of $C_4H_6Fe(CO)_3$: top, natural ^{13}CO content; bottom, ^{13}CO enriched.

The actual spectrum of $C_4H_6(CO)_3$ in the carbonyl region shows three strong bands at 2055.7, 1989.8, and 1979.9 cm^{-1} and three weak ^{13}CO bands at 2045 (sh), 1956.3, and 1945.9 cm^{-1}. This spectrum is shown in Figure 2. The presence of three strong carbonyl bands agrees with the assignment of C_s symmetry.

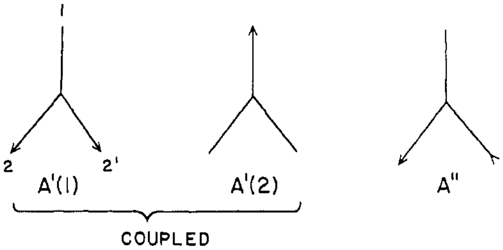
---

[10] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[11] For example: H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *ibid.*, **89**, 2844 (1967); F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, **6**, 1357 (1967); R. S. Gay and W. A. G. Graham, *ibid.*, **8**, 1561 (1969).

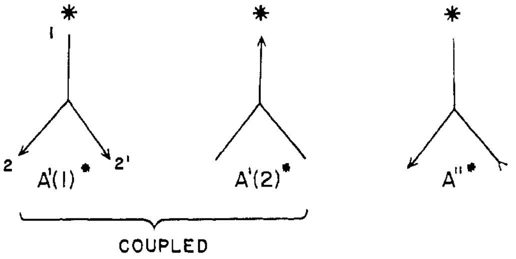
[12] See, for example, A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1964.

The forms for the tricarbonyl-^{12}C stretching vibrations may be represented by



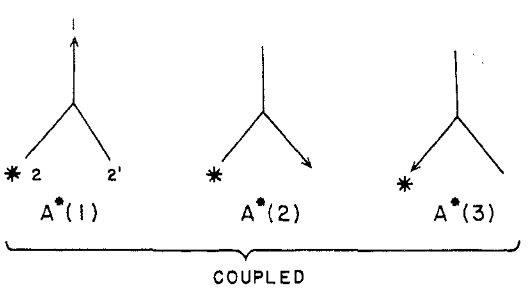
with symmetries of 2A′ and A″. The 2055.7-cm^{-1} value would be clearly assigned as one of the A′ vibrations (probably the A′(1)), but the assignment of the other two is uncertain.

If a ^{13}CO is substituted into the 1 position (designated by an asterisk), the molecular symmetry is still C_s, and the forms of the vibrations are the same, represented by



Owing to the change in the reduced mass and the coupling of the two A′* symmetries, these two bands will be shifted from the corresponding frequency in the ^{12}CO species. However, since A′*(1) is only a little changed from A′(1), its shift will be less than the shift of A′(2) to A′*(2). Since there is no ^{13}CO band with a relatively large shift from the 2055.7-cm^{-1} band, this verifies its assignment as the A′(1) vibration. Hence, one of the low-frequency ^{13}CO bands (1956.3 or 1945.9 cm^{-1}) must arise from A′*(2). The frequency of A″* should equal that of A″.

If the ^{13}CO is substituted into position 2, the symmetry is reduced to C_1. The forms of the vibrations of this species are



which represent three coupled A* vibrations. One of these bands must be the other low-frequency ^{13}CO band (1956.3 or 1945.9 cm^{-1}).

In solving for the force constants, the secular equations for the three species (tricarbonyl-^{12}C, 1-monocarbonyl-^{13}C, and 2-monocarbonyl-^{13}C) were written in the standard manner of Cotton and Kraihanzel.[10] This form has also been used by Van Hecke and Horrocks[13] for carbonyls not having octahedral geometry. Since four unknowns are to be determined, frequencies must be assigned to four vibrations. The four vibrations used were A′(1), which is known to be the 2055.7-cm^{-1} band, the other two ^{12}CO vibrations, having uncertain assignments as the 1989.8- and the 1979.9-cm^{-1} bands, and the A′*(2) vibration, being either 1956.3 or 1945.9 cm^{-1}. The other low-frequency ^{13}CO band will be one of the A* vibrations. Thus one has four permutations of the four assignments to be used in the calculation of four force constants. These force constants can then be used to calculate the position of the other ^{13}CO band as a check. In addition to the prediction of other ^{13}CO band positions, one has the relative sizes of K_1 to K_2 and K_{22}' to K_{12} as further checks.

The secular equations were solved on a CDC 6400 computer. The results are shown in Table III. It is clear that assignment III is superior to the other assignments. Not only are the force constants of the relative sizes expected, but all of the ^{13}CO vibrations occur at approximately the frequencies predicted.

Table III

Results of the Calculation of Force Constants and ^{13}CO Frequencies Using Various Assignment Permutations[a]

	Assignments			
	I	II	III	IV
A′(1)	2055.7	2055.7	2055.7	2055.7
A′(2)	1979.9	1989.8	1989.8	1979.9
A″	1989.8	1979.9	1979.9	1989.8
A′*(2)	1945.9	1945.9	1956.3	1956.3
	Calculated Values			
K_1	16.245	16.004	16.389	16.589
K_2	16.314	16.434	16.241	16.142
K_{12}	0.413	0.101	0.369	0.424
K_{22}'	0.329	0.608	0.415	0.157
Comment	$K_1 \ngtr K_2$ $K_{22} \ngtr K_{12}$	$K_1 \ngtr K_2$	As predicted	$K_{22} \ngtr K_{12}$
	Predicted Values			
A′*(1)	2045.0	2055.2	2044.3	2034.1
Comment	Obsd ~2045	Could be buried	Obsd ~2045	11 cm^{-1} off
A*(1)	2045.7	2039.4	2046.0	2050.1
Comment	Obsd ~2045	6 cm^{-1} off	Obsd ~2045	Could be buried
A*(2)	1983.0	1989.7	1987.5	1984.3
Comment	Buried	Buried	Buried	Buried
A*(3)	1952.0	1951.4	1947.1	1946.5
Comment	4 cm^{-1} off	5 cm^{-1} off	1 cm^{-1} off	1 cm^{-1} off

[a] Frequencies are in reciprocal centimeters and force constants in millidynes per ångström.

Enrichment of the ^{13}CO content is an ideally suited technique to test these assignments further. The shoulders may be clearly resolved and new bands for the disubstituted ^{13}CO species will appear.

The spectrum of $C_4H_6Fe(CO)_3$ after 60 hr of irradiation in the presence of 55% ^{13}CO is shown in Figure 2. The data of Table IV contain a comparison of the observed values with the calculated frequencies for the various species using assignment III of Table III. No other assignment comes close to giving this good an agreement.

These assigned values are more than a random selection of bands chosen in order to obtain the best agree-

---

(13) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

ment with predicted values. The order of band appearance and the relative intensities can be used to assign many bands to specific species. On the basis of the order of formation, the bands belonging to the two monosubstituted species can be readily sorted from the two disubstituted species. Further, the assumption of random substitution will lead to an expected yield of a 2:1 ratio of the 2-monocarbonyl-^{13}C species to the 1-monocarbonyl-^{13}C species and the same ratio of the 1,2-dicarbonyl-^{13}C species to the 2,2′-dicarbonyl-^{13}C species. This is consistent with the observation that the 2045.9- and 1945.9-cm^{-1} peaks assigned to the 2-monocarbonyl-^{13}C species are twice as intense as corresponding peaks assigned to the 1-monocarbonyl-^{13}C vibrations, 2043.9 and 1956.3 cm^{-1}. Although the dicarbonyl-^{13}C peaks predicted at 1965.4 and 1962.7 cm^{-1} were presumably not resolved, the other pairs of dicarbonyl-^{13}C peaks reflect a 2:1 ratio of 1,2-dicarbonyl-^{13}C to 2,2′-dicarbonyl-^{13}C.

Similar calculations have been made for the PF$_3$-substituted $C_4H_6Fe(CO)_3$ species. There are two ways that the structure of the monophosphine $C_4H_6Fe(CO)_2(PF_3)$ can be described. In one approach, the carbonyls are equivalent with PF$_3$ in the unique position, and in the other, the carbonyls are nonequivalent. One would expect two ^{12}CO bands and two ^{13}CO bands in the former case and two ^{12}CO and four ^{13}CO bands in the latter. The spectrum shows two ^{12}CO bands at 2031.6 and 1981.0 cm^{-1} and two weak ^{13}CO bands at 2017.6 and 1950.1 cm^{-1}. Although this would imply that the carbonyls are equivalent, two weak ^{13}CO bands could easily remain unseen.

The experimental data can be used to calculate the force constants for both situations. For the case of the equivalent carbonyls, the two ^{12}CO bands can be used to calculate the two force constants (one stretching and one interaction) and then predict the positions of the two ^{13}CO bands. In the case of the nonequivalent carbonyls, two ^{12}CO bands and one ^{13}CO band can be used to calculate the three force constants (two stretching and one interaction) and then predict the positions of the remaining three ^{13}CO peaks. It is interesting to note in the nonequivalent carbonyl case that the two stretching force constants were identical and the four ^{13}CO bands were predicted to fall in two pairs—each member of a pair being degenerate. Further the values of the force constants and the predicted ^{13}CO vibrations were identical with those calculated for the equivalent carbonyl case. All of this seems to suggest that PF$_3$ substitutes exclusively into the unique position. The values of the stretching and interaction force constants are 16.254 and 0.410 mdyn/Å, respectively. These force constants predict ^{13}CO values of 2017.5 and 1950.4 cm^{-1} which agree well with the observed values.

For the monocarbonyl $C_4H_6Fe(CO)(PF_3)_2$ the spectrum contains only two absorptions in the carbonyl region—a strong ^{12}CO band at 2001.4 cm^{-1} and a weak ^{13}CO band at 1956.3 cm^{-1}. One can calculate a force constant of 16.172 mdyn/Å. It is to be assumed from the work with $C_4H_6Fe(CO)_2(PF_3)$ that in $C_4H_6Fe(CO)(PF_3)_2$ the remaining carbonyl would be in one of the equivalent positions; that is, the phosphines are not equivalent. However, this phosphine nonequivalence is not necessarily proven from the infrared data.[13a]

TABLE IV

PREDICTED AND OBSERVED FREQUENCIES (CM^{-1}) FOR ^{13}CO-ENRICHED $C_4H_6Fe(CO)_3$ USING ASSIGNMENT III OF TABLE III

Vibration	Predicted	Obsd
	Tricarbonyl-^{12}C	
$A'(1)$	2055.7	2055.7
$A'(2)$	1989.8	1989.8
A''	1979.9	1979.9
	1-Monocarbonyl-^{13}C	
$A'^{*}(1)$	2044.3	2043.9
$A'^{*}(2)$	1956.3	1956.3
A''^{*}	Degenerate with A''	
	2-Monocarbonyl-^{13}C	
$A^{*}(1)$	2046.0	2045.9
$A^{*}(2)$	1987.5	*a*
$A^{*}(3)$	1947.1	1945.9
	2,2′-Dicarbonyl-^{13}C	
$A'^{**}(1)$	2034.8	2034.7
$A'^{**}(2)$	1965.4	*a*
A''^{**}	1935.7	1934.7
	1,2-Dicarbonyl-^{13}C	
$A^{**}(1)$	2031.2	2029.0
$A^{**}(2)$	1962.7	1963.3
$A^{**}(3)$	1941.9	1941.5
	Tricarbonyl-^{13}C	
$A'^{***}(1)$	2009.9	*b*
$A'^{***}(2)$	1945.4	*b*
A''^{***}	Degenerate with A''^{**}	

[a] Not resolved or buried. [b] Not enriched adequately to be observed.

The fluorine nmr investigation yielded some very interesting results. At room temperature, $C_4H_6Fe(CO)_2(PF_3)$ exhibits two sharp bands separated by 1300 Hz. This is interpretable as equivalent fluorines split by direct phosphorus coupling. Thus, there is support for the infrared evidence of PF$_3$ substitution into only one of the two types of positions, but the nmr data do not give any hint as to the location of that fluorophosphine group. Other than a slight shift to lower field, there is no change in the spectrum as the temperature is lowered to −100°.

The diphosphine complex $C_4H_6Fe(CO)(PF_3)_2$ gave a spectrum which was unexpected. As seen in Figure 3, the 30° spectrum consists of two parts—a sharp peak and a broad peak of some unresolved multiplet nature, separated by about 1300 Hz from a mirror image pattern of peaks. A spectrum of an exact mirror image set of peaks is interpreted[14] as being due to the presence of equivalent PF$_3$ groups and their concomitant second-order coupling. Yet, the force constant calculations indicated that the carbonyl was probably located in one of the equivalent sites which should mean nonequivalent phosphines.

(13a) NOTE ADDED IN PROOF.—With Bruker 90-MHz equipment, recently purchased in part with NSF funds, we have been able to show that in the spectra of $C_4H_6Fe(PF_3)_3$ new structure appears at low temperature as would be expected for two equivalent and one unique PF$_3$ group.

(14) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

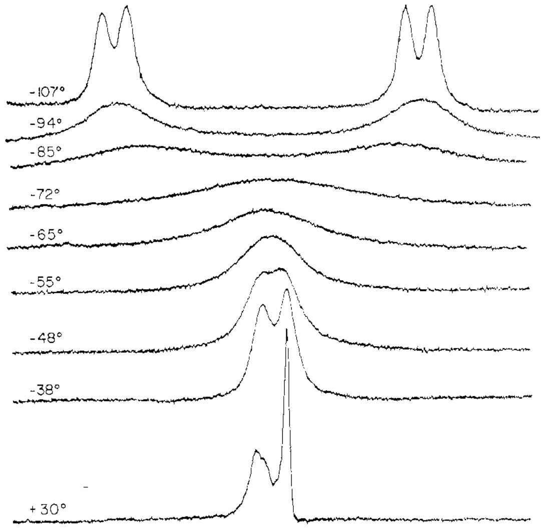


Figure 3.—The ^{19}F nmr spectrum of the low-field half of $C_4H_6Fe(CO)(PF_3)_2$. The upfield half is the mirror image of the low-field half. Separation of doublets in $-107°$ spectrum is 150 Hz.

Variable-temperature nmr illustrated in Figure 3 shows that at $-38°$ the spectrum begins to broaden and that by $-85°$ new structure is beginning to appear. By a temperature of $-107°$, the final spectrum shown in Figure 3 was obtained. This is interpretable as a first-order spectrum of two magnetically nonequivalent PF_3 groups with a chemical shift difference between them of about 150 Hz. In each group, the fluorine is subjected to direct phosphorus coupling of about 1300 Hz and to coupling with the neighboring phosphorus of about 10 Hz. The expected F–F coupling was not resolved at the temperatures reached.

The activation energy for the process has been calculated by the method of Muetterties and Phillips[15] and found to be about 6.7 kcal/mol.

The triphosphine shows a mirror image pattern at room temperature that is somewhat more complex than the corresponding diphosphine spectrum. Again, this type of pattern is indicative of equivalent PF_3 groups. At a temperature of $-50°$, the spectrum has begun to broaden but still has not completely collapsed at $-100°$. We have been unable to obtain a spectrum at a lower temperature with our present equipment.

Discussion

The carbonyl groups in butadieneiron tricarbonyl can either be exchanged with ^{13}CO or substituted by PF_3. These reactions occur either thermally or photochemically. The degree of butadiene replacement is quite low.

Spectroscopic analysis clearly shows that in solution, the carbonyl–phosphine sites are not equivalent. This is similar to the X-ray structure[3] in which the tricarbonyl moiety does not have a local C_{3v} symmetry. That one site is clearly different from the other two is shown by both force constant calculations on the tricarbonyl and fluorine nmr of the diphosphine.

In the tricarbonyl, $C_4H_6Fe(CO)_3$, the carbonyl infrared stretching region best fits a model having two stretching force constants and two interaction force constants. In $C_4H_6Fe(CO)_2(PF_3)$, the calculations indicate that the substitution yields exclusively the isomer in which the PF_3 group is in the unique position requiring only a single stretching force constant in the calculations.

Similarly, the low-temperature fluorine spectrum of $C_4H_6Fe(CO)(PF_3)_2$ shows that the three sites are not equivalent by yielding a spectrum in which the two PF_3 groups are clearly nonequivalent.

An unexpected phenomenon is the nmr equivalence of the PF_3 groups in $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ at room temperature. Both have spectra consisting of mirror image sets of peaks as is expected of equivalent PF_3 groups.[14] It seems clear that the equivalence is of a time-averaged variety rather than a basic structural change with temperature. With the triphosphine, it has not yet been possible to display the nonequivalence at low temperatures.

It is interesting to speculate on the nature of the motion that is responsible for this nmr equivalence. One possible mechanism would be the simple position exchange of the two phosphine groups. This implies that they are moving past one another by some form of bending motion. A more reasonable approach would be for the three ligands, the two phosphines, and the carbonyl to be undergoing rotation about a general axis as shown in Figure 4. Because the three sites are not mutually perpendicular, there would have to be some bending in addition to a rotation about the general axis. In concept, this motion is not unlike the Bailar twist.[16]

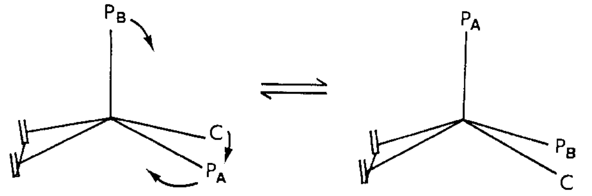


Figure 4.—Representation of a possible rotation mechanism for intramolecular exchange of phosphine groups.

There are three orientations of the three ligands. Two of these are equivalent with the carbonyl group being in one of the two basal positions, and in the third orientation the carbonyl is in the axial position. The low-temperature spectra show evidence for only the species in which the phosphines are nonequivalent. The motion could be one in which the ligands rotate back and forth between these two orientations. It is also possible that the rotation yields all three configurations. However, the energy of the configuration in which the carbonyl is in the unique location would then have to be sufficiently high so that the equilibrium concentration is too low to be detected. Only a few kilocalories difference in energy is needed to make the concentration of a minor constituent quite low.

---

(15) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(16) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967); J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

Since PF_3 and CO have been clearly demonstrated to be so similar,[7] it is quite reasonable to assume that the three carbonyl groups in $C_4H_6Fe(CO)_3$ are also undergoing a comparable motion. A similar situation could also occur in $C_4H_6Fe(CO)_2(PF_3)$, but with this species, the two configurations which place PF_3 in the equivalent positions would have sufficiently high energies so that their equilibrium concentration would be too low to be detected.

The fluxional nature of the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species was quite unexpected. Detecting this fluxional nature in the tricarbonyl would be difficult, but it becomes quite simple with the phosphorus trifluoride substituents. The phosphorus trifluoride ligand behaves as an excellent handle for CO in most situations.

From the published ^{13}CO nmr work on $C_4H_6Fe(CO)_3$,[17] it would be difficult to reach any conclusion relative to a fluxional nature of the compound.

Finally, if the model of a rotation of a group of three roughly orthogonal ligands is a generally correct mechanism for the internal motion in butadieneiron tricarbonyl, it seems quite likely that the same mechanism might be exhibited in other related species. The Berry model[18] has been assumed to be responsible for the stereochemical nonrigidity in trigonal-bipyramidal five-coordinate species. However, it also is reasonable to suppose that the rotation of a group of ligands located on two equatorial sites and an axial site could undergo a motion similar to that in the butadiene complex. We have tentative evidence that two different mechanisms of stereochemical nonrigidity are operative in the higher $CF_3Co(CO)_x(PF_3)_{4-x}$ species.[19]

It is felt that this mechanism requires a coordination number below 6 in order to be operative. A related mechanism for nondissociative exchange has been postulated for the six-coordinate octahedral species.[20] However, in compounds like $Mo(CO)_x(PF_3)_{6-x}$[21] and $R_fMn(CO)_x(PF_3)_{5-x}$,[22] there is no sign of isomerization among the species. In these, there may not be adequate room for the rotation to occur.

A referee has pointed out that there may be an analogy between the isomerization discussed by Nesmeyanov[23] in an allyl compound and that shown here. A rotation of the plane of the butadiene followed by a tilting of that plane is effectively the same motion that we have discussed, but approached from the other end of the molecule. It should be made clear, however, that there are no signs of nonequivalent rotation isomers for these butadiene complexes of the type found by Nesmeyanov.[23]

Acknowledgment.—J. D. W. wishes to thank the National Science Foundation for assistance in the form of an NSF traineeship. We also wish to thank the Atomic Energy Commission for financial assistance.

---

(17) H. G. Preston, Jr., Thesis, The University of Texas, Austin, Texas, 1965; H. F. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **88**, 2710 (1966).

(18) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(19) C. A. Udovich and R. J. Clark, to be submitted for publication.

(20) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

(21) R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

(22) W. J. Miles, Jr., and R. J. Clark, to be submitted for publication.

(23) A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Shchembelov, *J. Organometal. Chem.* (Amsterdam), **14**, 395 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Preparation and Properties of Some Oxygen-, Sulfur-, and Nitrogen-Bridged Phosphoryl and Thiophosphoryl Difluorides

BY T. L. CHARLTON AND R. G. CAVELL

Received June 27, 1969

The preparation and characterization of $(SPF_2)_2O$, $(SPF_2)_2S$, $(OPF_2)O(SPF_2)$, $(OPF_2)_2NCH_3$, $(SPF_2)_2NCH_3$, and the trimethylamine adducts $(OPF_2)_2NH\cdot(CH_3)_3N$ and $(SPF_2)_2NH\cdot(CH_3)_3N$ are described. Results of mass and infrared spectral studies are given. Reactions of the trimethylamine adducts with hydrogen chloride result in cleavage of the P–N bonds rather than liberation of the N–H compounds. The N–H compounds are observed, however, in the mass spectrometer.

Introduction

Many diphosphorus compounds are known in which the phosphorus atoms are linked by a difunctional bridging unit such as oxygen, sulfur, or monosubstituted nitrogen.[1-6] The only known pentavalent fluorophosphorus compounds of this type however are difluorophosphoric acid anhydride,[7,8] the analogous chlorofluoro compound,[9] and μ-oxo-bis(difluorophosphine).[10] Re-

---

(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950.

(2) M. L. Nielsen in "Developments in Inorganic Nitrogen Chemistry," Vol. 1, C. B. Colburn, Ed., Elsevier Publishing Co., Amsterdam, 1966, p 307.

(3) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960); **84**, 3442 (1962).

(4) (a) J. F. Nixon, *Chem. Commun.*, 669 (1967); (b) J. F. Nixon, *J. Chem. Soc.*, *A*, 2689 (1968); 1087 (1969).

(5) (a) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965); (b) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964).

(6) A. B. Burg and J. Heners, *J. Am. Chem. Soc.*, **87**, 3092 (1965); **88**, 1677 (1966).

(7) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

(8) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1960).

(9) C. Stölzer and A. Simon, *Chem. Ber.*, **94**, 1976 (1961).

(10) (a) M. Lustig, J. K. Ruff, and C. B. Colburn, *J. Am. Chem. Soc.*, **88**, 3875 (1966); (b) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *ibid.*, **88** 3729 (1966).